

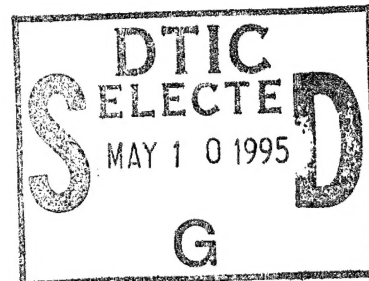
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ACIDITY AND BASICITY OF NITRO SUBSTITUTED IMIDAZOLES

T. Vladimiroff



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13. ABSTRACT (Maximum 200 words) The antibiotic azomycin is 2-nitroimidazole. 2,4-dinitroimidazole has recently been found to be a fairly powerful yet stable explosive. The family of all nitro substituted imidazoles constitute an interesting series of molecules from both the biological and the energetic material points of view. Imidazole is a heterocyclic five membered ring with two nitrogen atoms in the ring. One of these nitrogens is bound to a hydrogen atom so that it can act as a proton donor. The other nitrogen can act as a proton acceptor. The molecule can therefore act as both an acid and a base. In this work the protonation and deprotonation energies for all the nitro substituted imidazoles are computed with several basis sets. The GAUSSIAN 92 set of programs is used and all computations are performed at the SCF level of theory. The geometry of all the structures are determined using gradient techniques and compared to experimentally obtained geometries when available. It is found that these materials become more acidic and less basic as the degree of nitration increases.				
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INTRODUCTION

Azomycin, a naturally occurring antibiotic was found to be 2-nitroimidazole (ref 1). As is frequently done in biochemistry, once the structure of a biologically active molecule is determined, various derivatives are synthesized in order to modify its biological activity. Part of this synthesis activity resulted in the production of 2,4-dinitroimidazole (refs 2 through 5) and 4,5-dinitroimidazole (refs 2 and 5). These molecules were not found to be very interesting from the biological point of view. Recently, Dr. Damavarapu, of this laboratory, synthesized these materials and they were found to be fairly powerful yet stable explosives. One indication of this is that they are oxygen balanced to CO and water. The good stability can be expected since these materials are part of a family of heterocyclic, aromatic nitro compounds which were recently investigated by Vladimiroff (ref 6).

Imidazole is a heterocyclic five membered ring with two nitrogen atoms in the ring. The imidazole structure appears often in biological systems. One of the nitrogens is bound to a hydrogen atom so that it can act as a proton donor. The other nitrogen can act as a proton acceptor. The molecule can, therefore, act as both an acid and a base. Indications of this property can be seen in the crystal structure (refs 7 through 10) where imidazole compounds tend to hydrogen bond by way of the two ring nitrogens on two adjacent molecules. The x-ray structures of 2,4-dinitroimidazole (ref 9) and 4,5-dinitroimidazole (ref 10) have recently been determined by Dr. Bracuti of this laboratory. In this work, the structures of the various nitroimidazoles and polynitroimidazoles are computed using several basis sets and SCF theory and compared to the x-ray results. The protonation and deprotonation energies were determined by subtracting the energy of the parent molecule from the energy of the positive and negative ions. No attempt was made to correct the values to room temperature.

COMPUTATIONAL DETAILS

All the computations in this study were performed with the GAUSSIAN 92 (ref 11) system of quantum chemistry programs. Standard STO-3G, 4-31G, 6-31G, 4-31G*, and 6-31G* (ref 12) basis sets were used as indicated. Molecular geometries were determined by minimizing the total energy using gradient techniques. The force on each atom was reduced to less than 0.00045 a.u. The geometries of all the ions were optimized. No corrections were made for basis set superposition errors.

The standard notation for the imidazole ring is to label the nitrogen with the hydrogen on it as atom 1. The carbon between the two nitrogens is labeled atom 2 so that the nitrogen with no hydrogen becomes atom 3 and so forth around the ring. In

this work, an atom attached to a ring atom is given the same number as the ring atom thus N(2) is attached to C(2). There is no confusion since we do not consider the case where a like atom is attached to a ring atom. Each nitro group has two oxygen atoms attached to the nitrogen. For a nitro group next to a hydrogen, the oxygen nearest the hydrogen is labeled with an H, thus for 2-nitroimidazole the oxygen nearest the amine hydrogen is designated as O(2H). In the case of 4,5-dinitroimidazole, there is no hydrogen next to the nitro group in the 4 position. In this case, the oxygen on the same side as N(3) is labeled with a prime, thus it becomes O(4'). Tau is the twist angle by which the nitro groups are rotated out of the plane of the imidazole ring. They are labeled with the number of the atom to which the nitro group is attached.

RESULTS AND DISCUSSIONS

In the course of this investigation, the structure of all the nitro substituted imidazoles and their ions were computed. Several experimental x-ray structures are available in the literature. The comparisons between experimental and theoretical bond lengths and bond angles are made in tables 1 through 4. Theoretical errors are caused by the fact that the one-electron basis set is not complete and the fact that the electron correlation energy is not taken into account. The experimental geometries are affected by the thermal motion of the atoms, crystalline distortions of the molecule, and the fact that x-rays are sensitive to electron distributions rather than the actual position of the nuclei. In view of these observations, differences of 0.02 Å for bond lengths and 2 deg for bond angles should be considered acceptable.

The structure of 2-nitroimidazole was determined by Larsen (ref 7) at 105 K. The comparison between this work and our calculations are depicted in table 1. The agreement between theory and experiment is fairly good; however, several discrepancies can be noted. At the STO-3G level of theory several bond lengths are computed to be too long although the bond angles are reasonably well reproduced. Increasing the basis set size to 4-31G and 6-31G yields a marked improvement. Now all the theoretical bond lengths are in reasonable agreement with the experimental values with the exception of the N(2)-C(3) bond which is too short and the C-H and N-H bonds which are too long. The bond angles are in good agreement with experiment with the exception of the N(3)-C(2)-N(2) bond angle which is computed to be too big and the N(3)-C(4)-H(4) bond angle which is computed to be too small. The addition of polarization functions should improve the situation due to the extra flexibility in the basis set. Unfortunately, no such improvement was observed. In fact, for our best calculations at the 6-31G*/SCF level of theory, several bond lengths became considerably worse.

The C(2)-N(3) bond is now too short by 0.038 Å and the N-O bonds are also too short. The N-H and C-H bonds are still too long. This may be due to a shift of electron charge away from the proton and towards the ring. It seems that the addition of polarization functions on the first-row atoms does not significantly improve the accuracy of the bond length calculations. However, a slight improvement can be observed in the bond angle calculations when polarization functions are added, but in view of the experimental errors, this may not be physically significant.

Table 1
Calculated and experimental structure of 2-nitroimidazole

	<u>STO-3G</u>	<u>4-31G</u>	<u>6-31G</u>	<u>4-31G*</u>	<u>6-31G*</u>	<u>exp^a</u>
N(1)-C(2)	1.380	1.352	1.355	1.340	1.342	1.343
C(2)-N(3)	1.317	1.291	1.295	1.278	1.280	1.318
N(3)-C(4)	1.407	1.372	1.373	1.361	1.363	1.370
C(4)-C(5)	1.355	1.364	1.368	1.357	1.360	1.376
N(1)-H(1)	1.023	0.991	0.992	0.995	0.995	0.93
C(2)-N(2)	1.489	1.412	1.416	1.436	1.438	1.432
N(2)-O(2H)	1.285	1.239	1.241	1.200	1.202	1.235
N(2)-O(2)	1.274	1.210	1.213	1.181	1.183	1.226
C(4)-H(4)	1.079	1.061	1.063	1.068	1.069	0.93
C(5)-H(5)	1.080	1.063	1.064	1.067	1.068	0.92
N(1)-C(2)-N(3)	113.5	112.6	112.6	114.0	114.0	114.3
C(2)-N(3)-C(4)	103.3	105.6	105.5	104.4	104.4	103.8
N(3)-C(4)-C(5)	111.4	109.4	109.5	110.2	110.3	110.0
C(2)-N(1)-H(1)	125.4	125.1	125.0	125.4	125.4	125
N(3)-C(2)-N(2)	127.0	126.9	126.8	126.2	126.2	123.4
C(2)-N(2)-O(2H)	116.1	115.6	115.6	115.3	115.3	117.2
C(2)-N(2)-O(2)	118.4	119.4	119.5	118.3	118.4	117.8
N(3)-C(4)-H(4)	120.8	121.6	121.5	121.4	121.4	124.0
C(4)-C(5)-H(5)	131.9	131.4	131.4	132.0	132.0	131.0
tau(2)	0.0	0.0	0.0	0.0	0.0	0.0
energy	-422.6890	-427.6034	-428.0513	-427.8631	-428.2788	

Table 2
Calculated and experimental structure of 4-nitroimidazole

	<u>STO-3G</u>	<u>4-31G</u>	<u>6-31G</u>	<u>4-31G*</u>	<u>6-31G*</u>	<u>exp^b</u>
N(1)-C(2)	1.389	1.371	1.372	1.357	1.358	1.357
C(2)-N(3)	1.317	1.294	1.298	1.283	1.286	1.317
N(3)-C(4)	1.404	1.366	1.368	1.354	1.355	1.367
C(4)-C(5)	1.355	1.354	1.359	1.349	1.352	1.360
N(1)-H(1)	1.022	0.990	0.991	0.994	0.995	0.93
C(2)-H(2)	1.084	1.062	1.063	1.069	1.070	0.95
C(4)-N(4)	1.487	1.409	1.414	1.430	1.432	1.428
N(4)-O(4)	1.276	1.214	1.216	1.185	1.187	1.234
N(4)-O(4H)	1.284	1.237	1.239	1.199	1.201	1.236
C(5)-H(5)	1.081	1.061	1.063	1.065	1.066	0.94
N(1)-C(2)-N(3)	112.1	110.7	110.7	112.0	112.0	111.9
C(2)-N(3)-C(4)	103.4	105.6	105.5	104.4	104.4	103.6
N(3)-C(4)-C(5)	112.6	111.4	111.5	112.3	112.3	112.4
C(2)-N(1)-H(1)	126.6	126.2	126.1	126.4	126.4	125.0
N(1)-C(2)-H(2)	121.8	123.2	123.3	122.3	122.3	122.0
N(3)-C(4)-N(4)	121.4	123.0	123.0	122.8	122.8	120.7
C(4)-N(4)-O(2)	118.4	119.5	119.6	118.4	118.5	118.5
C(4)-N(4)-O(4H)	117.0	116.2	116.3	115.9	116.0	118.2
C(4)-C(5)-H(5)	131.9	131.1	131.2	132.0	132.0	131.0
tau(4)	0.0	0.0	0.0	0.0	0.0	0.0
energy	-422.6932	-427.6102	-428.0583	-427.8686	-428.2842	

(The energy is in Hartrees, the bond lengths are in Angstroms, and the bond angles are in degrees in both table 1 and 2.)

^a Data taken from ref 7.

^b Data taken from ref 8.

The x-ray structure of 4-nitroimidazole was determined by DeBondt, et al (ref 8). The comparison between the experimental data and our calculations is made in table 2. The results are very similar to those already observed with the 2-nitroimidazole. At the 6-31G level of theory the agreement with experiment is fairly good with the exception of the N-H and C-H bonds which are calculated to be too long. It is now the N(3)-C(4)-N(4) bond angle which is too big by 2.3 deg. The addition of polarization functions makes the N(2)-C(3) bond too short by 0.03 Å and the N-O bonds also become too short. There is no improvement in the length of the N-H and C-H bonds. The N(3)-C(4)-N(4) bond angle got slightly better and the C(4)-N(4)-O(4H) bond angles got slightly worse when polarization functions were added to the 6-31G basis set. Both molecules are predicted to be planar in agreement with the x-ray structures (refs 7 and 8).

The x-ray structure of 2,4-dinitroimidazole was solved by Dr. Bracuti (ref 9). This structure determination is characterized by relatively large standard deviations of 0.007 Å to 0.009 Å for the bonds involving first-row atoms (0.09 Å for the N-H bond and 0.08 Å for the C-H bond). The experimental bond lengths and bond angles determined for this molecule along with the theoretical counterparts are presented in table 3. Agreement with experiment does not seem to be as systematic as the two previous cases. With the exception of the STO-3G result, the N-H bond length is computed to be 0.1 Å shorter than experimental; however, this is almost within one standard deviation of the experimental value. The experimental C(2)-N(2) bond seems to be too long. These calculations indicate that it should be in the range 1.415 Å to 1.440 Å in better agreement with the value of 1.432 Å found for the 2-nitroimidazole. The relative lengths of the N-O bonds are somewhat unusual for the x-ray structure. The two N-O bonds in 2-nitroimidazole differ by 0.009 Å. The two N-O bonds in 4-nitroimidazole differ by 0.002 Å. However, the N-O bonds for the 2,4-dinitroimidazole differ by 0.037 Å for the nitro group in the 2 position and 0.035 Å for the 4 position. If all of the N-O bond lengths are averaged for the 2 and the 4 nitroimidazoles a value of 1.233 Å is obtained. This averaged value is substantially longer than the two experimentally obtained N-O values of 1.198 Å and 1.205 Å found in table 3. Since N-O bonds are quite strong and difficult to compress, it is hard to explain why these bonds are so short. The theoretical calculations also show fairly large variations in the lengths of the N-O bond with the largest being 0.03 Å for the nitro group on carbon 2. However, all the theoretical calculations predict that it is the N-O bond in proximity to the hydrogen which is the longest. This is in agreement with experiment for the nitro group on carbon 2, but disagrees with the experimental result for the nitro group on carbon 4. The bond angles do not agree very well with experiment with the largest deviation being for the amine hydrogen. The experimental value is 139 deg and the theoretical calculations are in the range 124.8 deg to 125.3 deg. This is probably due to the involvement of this hydrogen atom in hydrogen bonding. The theoretical calculations indicate that this molecule is planar while the x-ray structure show small rotations of the nitro groups out of the plane of the imidazole ring. These rotations are probably due to crystalline forces.

Table 3
Comparison of theoretical and experimental x-ray structure of 2,4-dinitroimidazole

	<u>STO-3G</u>	<u>4-31G</u>	<u>6-31G</u>	<u>4-31G*</u>	<u>6-31G*</u>	<u>exp^a</u>
N(1)-C(2)	1.385	1.359	1.362	1.342	1.349	1.363
C(2)-N(3)	1.317	1.286	1.290	1.274	1.276	1.286
N(3)-C(4)	1.401	1.356	1.358	1.347	1.348	1.338
C(4)-C(5)	1.362	1.364	1.368	1.358	1.360	1.370
N(1)-H(1)	1.025	0.994	0.994	0.997	0.997	1.10
C(2)-N(2)	1.492	1.415	1.419	1.438	1.440	1.471
N(2)-O(2H)	1.286	1.237	1.239	1.198	1.200	1.235
N(2)-O(2)	1.273	1.207	1.210	1.179	1.180	1.198
C(4)-N(4)	1.489	1.411	1.416	1.432	1.434	1.432
N(4)-O(4)	1.276	1.212	1.214	1.183	1.184	1.240
N(4)-O(4H)	1.284	1.235	1.237	1.197	1.199	1.205
C(5)-H(5)	1.082	1.062	1.064	1.066	1.067	1.08
N(1)-C(2)-N(3)	113.6	112.5	112.5	113.9	114.0	115.0
C(2)-N(3)-C(4)	102.4	104.6	104.5	103.4	103.4	101.4
N(3)-C(4)-C(5)	112.8	111.3	111.4	112.2	112.2	115.0
C(2)-N(1)-H(1)	125.1	124.8	124.8	125.2	125.3	139.0
N(1)-C(5)-H(5)	123.5	124.5	124.5	124.0	124.0	123.0
N(3)-C(2)-N(2)	127.1	127.1	127.0	126.3	126.2	123.8
C(2)-N(2)-O(2H)	115.6	115.1	115.1	114.8	114.8	114.7
C(2)-N(2)-O(4)	118.3	119.2	119.3	118.1	118.2	123.8
N(3)-C(4)-N(4)	121.3	123.1	123.1	122.8	122.8	121.5
C(4)-N(4)-O(4)	118.2	119.3	119.4	118.2	118.3	117.1
C(4)-N(4)-O(4H)	116.7	115.6	115.7	115.4	115.4	119.1
tau(2)	0.0	0.0	0.0	0.0	0.0	1.5
tau(4)	0.0	0.0	0.0	0.0	0.0	7.5
energy	-422.6932	-427.6102	-428.0583	-427.8686	-428.2842	

(The energy is in Hartrees, the bond lengths are in Angstroms, and the bond angles are in degrees.)

^a Taken from ref 9.

4,5-dinitroimidazole occupies two different crystallographic sites in the unit cell. As a result, two sets of slightly different geometric parameters are observed (ref 10) for this molecule. These distortions are probably caused by the crystalline field and are a measure of the extent to which the molecules can be distorted by the crystalline field. Unfortunately, this does complicate the comparison with the theoretical calculations since it is not possible to tell which value is closer to the undistorted value. For example, one of the C(2)-N(3) bonds seems to be too long (1.326 Å), the other C(2)-N(3) bond is in reasonable agreement with our 6-31G and 6-31G* calculations. The C-H and N-H bonds are always computed to be too long. One of the C(5)-N(5) bonds (1.447 Å) seems to be too long and is not in good agreement with our 6-31G and 6-31G* computations. The N-O bonds are found to be too short when the 6-31G* basis is used. All of our computed C(2)-N(1)-H(1) bond angles are between the two experimental values of 126 and 133 deg. However, all of the theoretical N(1)-C(2)-H(2) bond angles are found to be larger than the largest experimental value of 120 deg. There is not enough room to allow the two nitro groups on adjacent carbons to lie in the plane of the imidazole ring so that both nitro groups are twisted out of the plane

of the ring. Both theory and experiment agree on this point. For the nitro group on C(5), all of the calculated torsional angles lie between the experimental values, but for the other nitro group the computed torsional angle is too large.

Table 4
Comparison of theoretical and experimental X-ray structure of 4,5-dinitroimidazole

	STO-3G	4-31G	6-31G	6-31G*	experimental ^a	
					(1)	(2)
N(1)-C(2)	1.380	1.346	1.348	1.336	1.346	1.329
C(2)-N(3)	1.325	1.310	1.314	1.300	1.316	1.326
N(3)-C(4)	1.398	1.349	1.352	1.339	1.355	1.352
C(4)-C(5)	1.362	1.357	1.360	1.354	1.357	1.355
N(1)-H(1)	1.025	0.994	0.994	0.997	0.86	0.87
C(2)-H(2)	1.085	1.062	1.063	1.069	0.97	0.90
C(4)-N(4)	1.495	1.428	1.432	1.448	1.452	1.449
N(4)-O(4')	1.278	1.217	1.219	1.188	1.221	1.220
N(4)-O(4)	1.280	1.220	1.222	1.189	1.214	1.212
C(5)-N(5)	1.487	1.405	1.408	1.422	1.447	1.426
N(5)-O(5)	1.274	1.213	1.216	1.186	1.209	1.219
N(5)-O(5H)	1.286	1.235	1.237	1.199	1.224	1.229
N(1)-C(2)-N(3)	112.2	110.7	110.8	112.2	112.7	112.4
C(2)-N(3)-C(4)	104.2	106.3	106.1	105.2	104.7	104.0
N(3)-C(4)-C(5)	111.3	110.1	110.2	110.9	110.4	111.2
C(2)-N(1)-H(1)	129.0	128.6	128.5	128.8	126	133
N(1)-C(2)-H(2)	122.0	123.8	123.8	122.7	117	120
N(3)-C(4)-N(4)	120.0	119.8	119.8	119.8	118.6	118.7
C(4)-N(4)-O(4')	117.0	117.0	117.0	116.2	116.8	117.4
C(4)-N(4)-O(4)	117.8	117.3	117.3	116.9	118.5	118.4
C(4)-C(5)-N(5)	135.5	134.8	134.6	134.5	136.1	133.8
C(5)-N(5)-O(5)	118.8	118.8	118.7	117.8	118.0	118.4
C(5)-N(5)-O(5H)	115.5	115.8	116.0	115.6	116.8	117.2
tau(4)	34.4	50.4	53.4	54.6	16.7	27.8
tau(5)	9.1	8.2	8.1	7.8	5.9	17.0
energy	-623.381	-630.718	-631.376	-631.728		

^a Taken from ref 10.

Finally, attention is turned to the calculation of the difference in energy between the parent molecule and the various positive and negative ions. Unlike the usual case where ions are formed by adding or subtracting electrons, here the negative ion is formed by removing a proton from N(1) or the positive ion by adding a proton to N(3). Since no real advantage could be demonstrated for known structures of the nitroimidazoles by going to a polarized basis set and because of the increase in computer time required by calculations with the polarized basis, these calculations were carried out without polarization functions. Similar calculations for the protonation reaction were reported for the methyl substituted imidazoles by Catalan, et al (ref 13). Jaimenz, et al (ref 14) reported protonation energies for the 2-nitroimidazole and the 5-nitroimidazole using a 6-31G basis set. The structure of each ion was fully optimized. The results are reported in table 5 along with some data available in the literature (refs 13 and 14). The deprotonation energy is essentially the energy required to remove the proton on N(1). As this value decreases, the proton is removed more easily which implies that the molecule is more acidic. The protonation energy is the energy gained when a proton is substituted on N(3). As this value decreases, less

energy is gained and the material becomes less basic. From the values in table 5, it can be seen that as nitro groups are added to the imidazole ring, imidazole becomes more acidic and less basic. STO-3G energy differences are quite a bit larger than the 4-31G and 6-31G values which are in good agreement with each other. Going to larger basis sets could influence the individual numbers but should preserve the general trend.

Table 5
Acidity and basicity of nitro substituted imidazoles in kcal/mole

Compound	Deprotonation			Protonation		
	STO-3G	4-31G	6-31G	STO-3G	4-31G	6-31G
imidazole	436.9	376.4	374.2	283.3 283.5 ^a	247.9 246.8 ^a	247.0
4-nitro	408.0	344.1	342.4	264.2	223.3	222.6 222.7 ^b
2-nitro	406.4	345.2	343.2	262.6	219.3	218.6
5-nitro	406.1	343.6	341.9	266.1	223.8	223.1 223.2 ^b
2,4-dinitro	382.4	319.4	317.9	245.8	196.7	196.3
2,5-dinitro	380.3	316.9	315.5	247.9	199.2	198.7
4,5-dinitro	384.6	321.2	319.7	251.5	204.9	203.9
2,4,5-trinitro	361.7	296.5	295.1	235.0	181.8	180.9

^a Taken from ref 13.

^b Taken from ref 14.

CONCLUSIONS

The structure and energy of various nitroimidazoles and their positive and negative ions were computed using ab initio methods. Known x-ray structures were compared with the theoretical geometric parameters. It was observed that the addition of polarization functions did not significantly improve the accuracy of the calculated bond lengths. Generally speaking, the theoretical C-H and the N-H bonds were found to be too long. The N-O bonds were computed to be too short, if polarization functions were used. The over all agreement between theory and experiment seemed to be worse for the 2,4-dinitroimidazole. Imidazoles become more acidic and less basic as nitro groups are added to the ring. This is in contrast with the case where methyl groups are substituted on the imidazole ring which produces very strong gas-phase basicity.

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